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Crystallization Process of a $\text{LiTaO}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ Glass

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A transparent glass-ceramic containing ferroelectric LiTaO_3 crystals is obtained from a glass of the composition 65mol% LiTaO_3 , 17.5 $\text{AlO}_{1.5}$, 17.5 SiO_2 , by heating from room temperature to 900°C at a rate of 5°C/min. To study effects of a metastable liquid-liquid phase separation on the subsequent crystal nucleation, structural changes of the glass during heat-treatment were investigated. The phase separation occurred from about 800° to 840°C. In its early stage (near 800°C), the phase-separated structure exhibited a microheterogeneity on 10 nm scale, whereas, in its advanced stage, it changed into a coarser structure composed of glassy droplets 0.5~1 μm in diameter, large enough to scatter the visible rays. The specimen with such a coarse structure showed opalescence. At 850°C, the opalescence disappeared. From 850°C, the glass started to crystallize, but remained transparent, at least, up to 900°C because the size of the individual crystal particles precipitated was less than 10 nm, small enough to minimize light scattering. The slow heating from 780° to 810°C which corresponded to the early stage of phase separation was found necessary to make the resulting glass-ceramic transparent. It was concluded that the phase separation in its early stage enhanced the crystal nucleation.

I. INTRODUCTION

Transparent glass-ceramics containing a large amount of LiTaO_3 crystals can be obtained from glasses of the $\text{LiTaO}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system by heat-treatments^{1,2)}. The present authors found that, during the heat-treatment, some of the glasses of this system developed opalescence in a short temperature range before they transformed into transparent aggregates of crystals. The cause of the development of the opalescence and its effect on the subsequent crystallization were investigated for a glass of the composition, 65 mol % LiTaO_3 , 17.5 $\text{AlO}_{1.5}$, 17.5 SiO_2 .

II. EXPERIMENTAL

1. Preparation of Glass

A batch of 15 g yielding a glass of the composition, 65 mol% LiTaO_3 , 17.5 $\text{AlO}_{1.5}$, 17.5 SiO_2 was prepared from reagent-grade Li_2CO_3 , Ta_2O_5 , $\text{Al}(\text{OH})_3$, and SiO_2 . It was melted in a Pt crucible at 1550°C for 1 h in a furnace heated electrically with SiC elements. The melt was poured onto a steel plate and pressed into a plate of about 1 mm thick. The resulting glass was transparent and colorless.

2. Heat-Treatment of Glass

The chilled glass plate was cut into squares of approximate dimensions of 5 by 5 by 1 mm, placed on a platinum plate and subjected to the following heat-treatments:

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Method A The specimen is heated at a rate of $5^{\circ}\text{C}/\text{min}$ from room temperature to various temperatures in a range of 800° to 900°C in an electrically heated furnace and immediately taken out from the furnace to be allowed to cool in air.

Method B-I The specimen is inserted into the furnace previously kept at 780°C . By this procedure the temperature of the specimen could be raised to 780°C within about one min. Then, the specimen is further heated to various temperatures in a range of 800° to 900°C at a rate of $5^{\circ}\text{C}/\text{min}$ and finally taken out from the furnace to be allowed to cool in air.

Method B-II The specimen is inserted into the furnace previously kept at 810°C . Then, the specimen is further heated to various temperatures in a range of 830° to 900°C at a rate of $5^{\circ}\text{C}/\text{min}$ and finally taken out from the furnace to be allowed to cool in air.

The photograph in Fig. 1 show transparency of the specimens heat-treated by the various methods. Temperatures indicated in Fig. 1 denote the maxima from which the specimens were cooled in air.

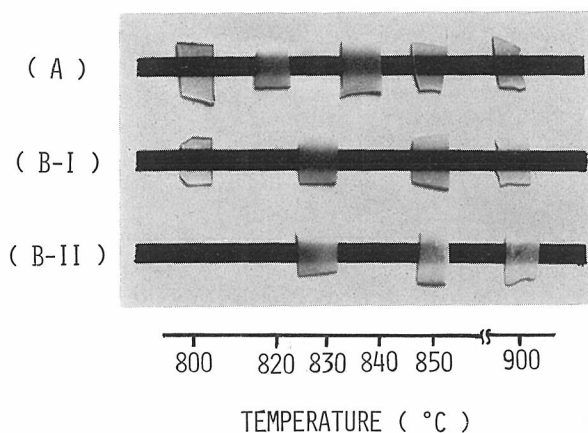


Fig. 1. Transparency of the specimens subjected to various heat-treatments. (A) heated from room temperature to the temperatures indicated at a rate of $5^{\circ}\text{C}/\text{min}$, (B-I) heated from room temperature to 780°C within about 1 min and thereafter to the temperatures indicated at a rate of $5^{\circ}\text{C}/\text{min}$, (B-II) heated from room temperature to 810°C within about 1 min and thereafter to the temperatures indicated at a rate of $5^{\circ}\text{C}/\text{min}$.

3. X-Ray Diffraction Analysis

The specimens heat-treated by the various methods were subjected to powder X-ray diffraction analysis. No crystal was identified in any of the specimens heated below 850°C whereas LiTaO_3 crystals with a perovskite-type structure were found to precipitate in the specimens heated over 850°C .

4. Electronmicroscopic Observation

The surfaces of the specimens heat-treated by Method A were ground and polished with Al_2O_3 and CeO_2 powders, successively, to a depth of about 0.2 mm

from their original surfaces, followed by immersion in 5% HF solution 1~15 min. Platinum-palladium pre-shadowed carbon replicas of the HF-etched surfaces were examined in a electronmicroscope (Hitachi Ltd, Model HU-11D-1). The microphotographs are shown in Fig. 2.

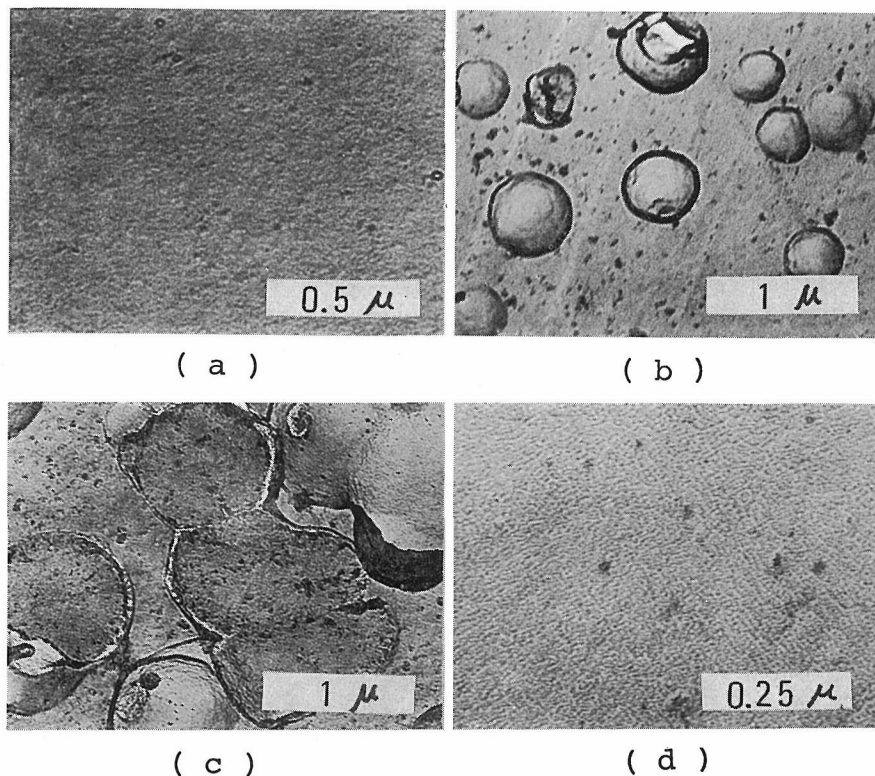


Fig. 2. Electron micrographs of the glasses heated to (a) 800°C (b) 820°C (c) 840°C and (d) 850°C respectively, at a rate of 5°C/min.

III. DISCUSSION

The result shown in Fig. 1 (A) indicates that in the process of heat-treatment by Method A opalescence develops in the glass in the range from 820° to 840°C. Since precipitation of LiTaO₃ crystals in the glass starts from 850°C (II. 3), the opalescence is assumed to be a result of the metastable liquid-liquid phase separation. The electronmicrographs shown in Fig. 2 support this assumption: The micrographs for the two specimens heated to 820° and 840°C, respectively, show a typical pattern of the phase-separated microstructure, especially in the advanced stage of phase separation, in which one glassy phase in the form of discrete droplets had already grown up to the size large enough to scatter the visible rays; *i.e.*, about 0.5 and 1 μm in diameter for the specimens heated to 820°C and 840°C, respectively. The origin of the phase-separated structure described above may be traced back to a structure observed in the micrograph for the transparent specimen heated to 800°C

(Fig. 2, (a)), which shows microheterogeneity on the 10 nm scale. Therefore the range from 800°C to 820°C may be called as the early stage of phase separation.

When the opaque specimen is further heated to 850°C, it regains transparency (Fig. 1, (A)). In this stage, no glassy droplet remains but minute particles, about 10 nm in diameter, identified as the LiTaO_3 crystal by X-ray analysis precipitate in the specimen (Fig. 2, (d)). The crystals particles were about 10 nm in diameter which is small enough to minimize light scattering. The transparency of the specimen is thus attributed to the extraordinarily small size of its constituent LiTaO_3 crystal particles. Disappearance of the phase-separated structure at about 850°C indicates that this temperature corresponds approximately to the clearing temperature of the glass; the upper limit of the temperature region of phase separation.

The results shown in Fig. 1 (B-I) and (B-II) provide a basis for discussing the effects of the phase separation on the rate of subsequent crystal nucleation in the glass: The glass specimen, when heated rapidly from room temperature to 780°C and then at a rate of 5°C/min to higher temperatures (Method B-I), develops opalescence at about 830°C, and then, transforms into a transparent glass-ceramic from about 850°C (Fig. 1, (B-I)). The specimen, when heated rapidly to 810°C and then at a rate of 5°C/min to higher temperatures (Method B-II), also develops opalescence at about 830°C, but does not transform into a transparent glass-ceramic; without regaining transparency, it transforms into an opaque glass-ceramic containing large crystal particles capable of light scattering (Fig. 1, (B-II)). The big difference in process of heat-treatment between the Method B-I and B-II is that the slow heating at a rate of 5°C/min in the range from 780° to 810°C is absent in the latter process. Since this temperature range corresponds to the early stage of phase separation, it is concluded that the early stage of phase separation is a necessary step for the formation of the transparent glass-ceramic. It is apparent from the experiment shown in Fig. 1 (B-II) that the phase separation in an advanced stage, in which the glassy droplets have already grown up so large that the shows opalescent, is of no use for obtaining the transparent glass-ceramic.

Generally, the glasses from which transparent glass-ceramics are easily obtained have a strong tendency to show, on heating, a phase separation at a very fine scale, especially in its early stage. Glasses in the $\text{PbTiO}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ ³⁾ and $\text{Li}_2\text{O-SiO}_2\text{-Al}_2\text{O}_3\text{-TiO}_2(\text{ZrO}_2)$ ^{4,5)} systems are the examples. The present authors also reported elsewhere that in the $\text{LiTaO}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system, too, the compositional region from which transparent glass-ceramics are easily obtained coincides well with the region in which the glasses show a phase separation at a very fine scale similar to that observed in the early stage of the phase separation in the glass examined in the present study.

In a study of binary lithium silicate glasses of composition from 27.4 to 32.5 mol% of Li_2O , Tomozawa⁶⁾ concluded that in early stages of phase separation crystalline nucleation was accelerated. He suggested that the diffusion zone around the growing silica particles might be favorable region for crystalline nucleation. For the glass examined in the present experiment, the similar condition favorable for sub-

sequent crystalline nucleation might be set up in the early stage of the phase separation.

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